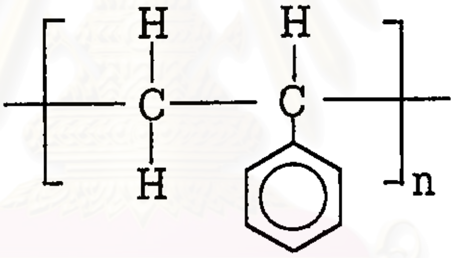
CHAPTER III

THEORY

3.1 Polystyrene (PS)

The basic polymer unit of polystyrene is based on the ethylene chain and has the following structure:



Commercial polystyrene is produced by bulk polymerization, suspension polymerization and solution polymerization techniques or by combining various aspects of these techniques. The polymerization is a highly exothermic, free radical reaction[Harper, 1975]. The homopolymer is the noncrystallizing type, with glass transition temperature (T_g) approximately 100°C [Birley, 1988]. The low T_g and the amorphous nature of the PS mean that PS is one of the easiest plastic to mould, since the adjustment of manufacturing process temperature may be used to reduce the viscosity to processable levels. However, PS tends to degrade by depolymerization at temperature above 150°C so long dwell times in the melt should be avoided.

Below its T_g, it is a very stiff but brittle and highly transparent (clear) glassy material. It has poor weatherability and can be chemically attacked by oils and organic solvents. Resistance is good, however, to water, inorganic chemicals, and alcohols.

Processing of polystyrene is generally straightforward. Many common processes can be applied which include injection molding, with corresponding easy flowing grades, extrusion of finished products (profiles, pipes, sheets which can be subsequently thermoforming) [Charrier, 1990].

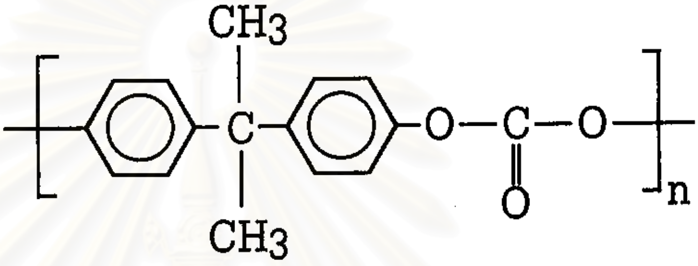
Polystyrene is commercially available in a number of grades as follows [Harper, 1975]:

1. General-purpose type
2. Impact grade: rubber-filled polystyrene
3. Chemical-resistant grades: copolymers of styrene and acrylonitrile
4. Specialty grades: light-stabilized styrene-methyl methacrylate copolymer for weathering and glass-reinforced polystyrenes

Polystyrene used in this study is the general-purpose polystyrene resin. The commercial success of polystyrene is largely due to transparency, colorless, ease of fabrication, thermal stability, low specific gravity, relatively high modulus, excellent electrical properties, and low cost. Typical applications for general-purpose polystyrene resins include packaging products, disposable medical ware, toys, tumblers and consumer electronics. Foam applications include egg cartons, meat-packaging trays, and building insulation [Jacqueline, 1990].

3.2 Poly(bisphenol A carbonate) (PC)

This group of plastic is also among those which are classified as engineering thermoplastic because of their high performance characteristics in engineering applications. The general chemical structure is shown belows:



Polycarbonate is especially outstanding in impact strength. The impact strength is much higher than other engineering thermoplastics [Harper, 1975]. Polycarbonate is tough, rigid, and dimensionally stable and available as transparent or colored They are easily fabricated with reproducible, using molding or machining techniques. Polycarbonate is resistant to oxidation in air at elevated temperatures.

The deformation properties of PC are not particularly sensitive to temperatures until the softening region (T_g) above 150°C is reached [Birley, 1988]. Compared with PS, the melt is processed at higher temperature corresponding to the T_g of PC which is 50°C higher than PS.

Polycarbonate is usually used in electrical applications, household and consumer articles, automotive applications, photographic and optical equipment, sporting goods, construction, medical applications, packaging, laser-optical data-storage systems, and films [Jacqueline, 1990].

3.3 Liquid Crystal

3.3.1 Definition of a liquid crystal

A liquid crystal is a simple state of matter between the crystal and the liquid states that can exhibit long-range order in one or two dimensions only [Sperling, 1992; Folkes and Hope, 1993].

The liquid crystalline state was first observed by Austrian botanist, Friedrich Reintzer, in 1888 [Cowie, 1991]. He found that cholesteryl esters formed opaque liquids on melting which, on heating to higher temperature, subsequently cleared to form isotropic liquids. This behaviour was interpreted by Lehmann as evidence for the existence of a new phase lying between the solid and isotropic liquid state [Cowie, 1991]. This new state was known as a mesophase, from the Greek mesos meaning "in-between" or "intermediate" by Fridel [Cowie, 1991]. These mesophases are quite fluid but also show birefringence. They appear to have properties associated with both crystal and liquid, so they were called "liquid crystal" by Lehmann [Cowie, 1991].

Many natural materials can exist in the liquid crystal state. Examples of common materials include DNA, cholesterol, and tobacco mosaic virus. The best known synthetic liquid crystals are those used in liquid crystal displays.

Both small molecules and polymers may exist in the liquid crystalline state, but generally special chemical structures are required, i.e. the chemical structure composes of a central core comprising aromatic or cycloaliphatic units joined by rigid links, and has either polar, or flexible alkyl and alkoxy terminal groups. Some typical examples of possible small molecule structures that form liquid crystalline state are shown in Table 3-1 and these units are called "mesogens".

3.3.2 Liquid Crystal Classification

There are three main types of liquid crystal according to their structures as classified by Friedel [Folkes and Hope, 1993]:

1. Nematic

Molecules in the nematic state, Figure 3-1a, is ordered in one dimension only. The chains lie parallel to each other at equilibrium. The nematic state is the least ordered liquid crystalline phase. Nevertheless, the nematic state is more ordered than the isotropic state (which is a normal state of fluid), as shown in Figure 3-1d.

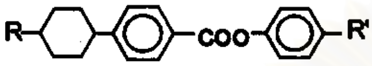
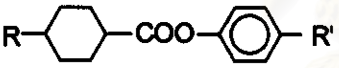
2. Smectic

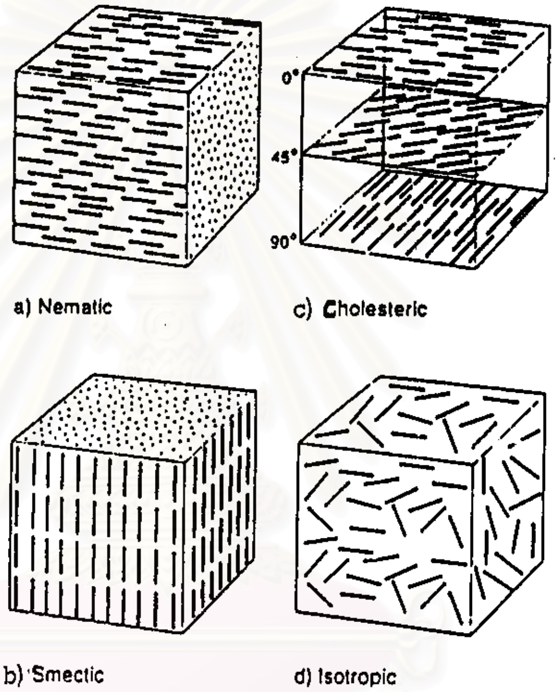
Molecules in the smectic phase is ordered in two dimensions, as shown in Figure 3-1b.

3. Cholesteric

Molecules in the cholesteric mesophase are twisted structures, as shown in Figure 3-1c.

Table 3-1 The examples of mesogens [Merck, 1985].

Mesogen	R group
	R = —C_3H_7 ; R' = —C_3H_7 = —C_3H_7 ; = —C_5H_{11} = —C_5H_{11} ; = —C_3H_7 = —C_2H_5 ; = —CN = —C_5H_{11} ; = —CN
	R = —C_3H_7 ; R' = —C_3H_7 = —C_3H_7 ; = —C_5H_{11} = —C_4H_9 ; = —C_4H_9 = —C_5H_{11} ; = —C_3H_7 = —C_5H_{11} ; = —C_5H_{11}
	R = —C_5H_{11} ; R' = —C_5H_{11} = —C_3H_7 ; = —OCH_3 = —C_3H_7 ; = —OC_2H_5 = —C_3H_7 ; = —OC_4H_9 = —C_4H_9 ; = —OCH_3 = —C_4H_9 ; = —OC_2H_5 = —C_5H_{11} ; = —OC_4H_9



a) Nematic
c) Cholesteric
b) Smectic
d) Isotropic

Figure 3-1 Main classification of liquid crystalline phase [Folkes and Hope, 1993].

It is also possible to classify liquid crystal into two main classes according to the formation of liquid crystalline state:

1. Thermotropic

The phase change of the liquid crystal from crystal to liquid crystal can be achieved by heating.

2. Lyotropic

The phase change of the liquid crystal from crystal to liquid crystal can be achieved by dissolution.

3.3.3 Mesophasic Transition Temperature

The various transitions that liquid crystal undergo as the temperature increases from the most ordered to the least ordered states, can be shown as belows:

$$\text{crystal} \rightarrow \text{smectic(S)} \rightarrow \text{nematic(N)} \rightarrow \text{isotropic}$$

The temperature at which liquid crytsal changes from crystal to the first liquid crystalline phase is called "crystalline melting temperature".

The temperature at which liquid crystal changes from smectic phase to nematic phase is called "S → N transition temperature ($T_{S \rightarrow N}$)".

The temperature at which the last (or only) liquid crystalline phase gives way to the isotropic melt or solution is called "clearing temperature".

The examples of mesophasic transition temperature of HP35 and HP5N (two low molar mass used in this study) are shown below:

1. HP35

HP35 exhibits a crystalline melting transition at 80°C and the S → N transition temperature ($T_{S\rightarrow N}$) at 87°C. HP35 exhibits the state change from the nematic to isotropic (clearing temperature) at 176°C [Merck, 1996].

$$\text{crystal} \xrightarrow{80^{\circ}\text{C}} \text{smectic(S)} \xrightarrow{87^{\circ}\text{C}} \text{nematic(N)} \xrightarrow{176^{\circ}\text{C}} \text{isotropic}$$

The structure of HP35 is shown in Figure 4-3.

2. HP5N

HP5N melts to a nematic state at 111°C and becomes an isotropic liquid (clearing temperature) at 226°C [Merck, 1996].

$$\text{crystal} \xrightarrow{111^{\circ}\text{C}} \text{nematic(N)} \xrightarrow{226^{\circ}\text{C}} \text{isotropic}$$

The structure of HP5N is shown in Figure 4-4.

3.4 The Preparation of the Blends

Preparation of polymer blends can be accomplished by several methods [Walsh, 1985].

3.4.1 Melt Mixing

Melt Mixing is done by mixing the mixture in the melt state. Mixing in the melt state is the method of choice for the preparation of polymer blends in a large scale. The advantage of this method is the free from foreign components (e.g., solvents) in the blend.

The disadvantage of melt mixing is that both components must be in the molten state, which can mean that temperature may be high enough to cause degradation. Mixing equipment for melts invariably involves metal surfaces which move in opposition; for this reason, bearings and seals are always required. Another disadvantage of melt mixing is the cost of the equipment. Also, even laboratory-size mixing equipment generally works well only with large amounts of material; e.g., 50 grams or more. If mixing quantities of less than 1 gram is required, melt mixing is hardly feasible.

For laboratory-scale mixing, a number of devices are available. For example: electrically heated two-roll mill, brabender mixer, extruder, rotational rheometer.

3.4.2 Casting From Common Solvents

This method is done by dissolving the mixture in the suitable solvent and then removing the solvent from the mixture.

Casting of the blends from a common solvent is the simplest mixing method available and is widely practiced in a laboratory scale. Very small quantity of experimental polymers can be handled easily. The resulting product, a film, is immediately useful for thermal analysis, dynamic mechanical analysis, etc. If pure solvents and clean glassware are used, contamination can be precluded. In most cases, temperatures never exceed ambient, so degradation is not a problem.

The most severe problem with casting is the influence of the solvent and the casting history on the resulting product. In spite of the fact that most of the solvent can be removed from a cast film, the nature of the film depends strongly on the solvent and the conditions used during casting.

To avoid concentration and temperature gradients during the removal of solvent, casting is best done in thin films and with slow solvent removal.

There are a number of methods for casting thin films from polymer solutions. One easy method is to spread the solution over a glass plate by rolling a rod wound with wire through a puddle of the syrup. Most researchers simply cast dilute solutions into flat dishes. If films at very uniform thickness are needed, the solution can be cast onto mercury. Covering the cast solution with an inverted dish slows the evaporation of the solvent and promotes uniform films.

3.4.3 Freeze Drying

In the freeze drying process a solution of the two polymers is quenched down to a very low temperature and the solvent is frozen. Solvent is then removed cleanly by sublimation. Dilute solutions must be used and the solution volume must be kept low for good heat transfer.

An advantage of this method is that the resulting blend will be independent of the solvent. Freeze drying seems to work best with solvents having high symmetry, i.e. benzene, dioxane, naphthalene, etc. This is also the limitation of this method.

3.4.4 Emulsions

The handling polymers as emulsions has many advantages as same as the use of solution casting. Films can be casted; mixing requires no expensive equipment; high temperature is not needed.

Emulsions of polymers are not always available or easy to make. While emulsion polymerization is highly advanced, it is not applicable to all monomers.

3.4.5 Mixing via Reaction

Co-crosslinking and interpenetrating polymer networks (IPN) formation are specialty methods for forming blends. The idea of these methods is to force a degree of miscibility by reactions between the polymers.

3.5 Miscibility Characteristics of the Blends

Mixing is the process that makes blends by putting several components together so that the blends become homogeneous or heterogeneous with small domain sizes. Blends can be classified into three categories [Thongyai, 1990] as belows:

1. Miscibility

Miscibility is the state of a single phase where the level of molecular mixing is adequate to yield macroscopic properties expected of single phase material [Olabisi, 1979].

2. Partial miscibility

Partial miscibility exhibits at least two miscible phases where each phase may comprise a high concentration of one component with a smaller dissolved portion of the other.

3. Immiscibility

Immiscibility is a state of two phases in which each phase comprises of individual component and exhibits both macroscopic and/or microscopic properties of that component.

Miscibility characteristic mainly depends on several parameters such as compositions, methods of mixing, temperature, pressure and volume of mixing.

3.5.1 Gibb's Free Energy and Miscibility Characteristics

The miscibility of a mixture is determined by the Gibbs' free energy of mixing (ΔG_m), which is related to the entropic (ΔS_m) and enthalpic (ΔH_m) components through the simple relation.

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (3\text{-}1)$$

After blending, the value of free energy and other thermodynamics properties of the blend may be changed from properties of the pure component. In general, the systems will change to an equilibrium condition of the lowest possible free energy. In other words, the system will be most likely to be more chaotic (more entropy) and has less internal energy (less enthalpy). Thus, the first criteria of miscibility is that the free energy of mixing must be less than zero. This criteria can be written as belows:

$$[\ \Delta G < 0\ ]_{\text{Temperature, Pressure, Compositions}} \qquad (3\text{-}2)$$

3.5.2 The Phase Diagram of Polymer Blends

For general usage, if the phase separation curves are available, the working conditions and the processing parameters of the blend can be properly determined. The phase separation curve can be obtained from the diagram called "Phase Diagram" which usually is a plot of temperature versus composition of the blend. Pressure and other process parameters also have some effects on phase separation, but these parameters hardly change in normal ambient conditions. In real polymer blend systems, many types of phase diagrams can be found as shown in Figure 3-2 [Kroschwitz, 1990]. The shade area in Figure 3-2 represents phase separation. The unshaded area area in Figure 3-2 represents homogeneous region.

Figure 3-2a shows the upper critical solution temperature (UCST) behaviour of a typical polymer blends in which an initially homogeneous mixture undergoes phase separation upon lowering of temperature (increasing temperature increase miscibility) [Paul and Newman, 1978].

When the blend goes from one phase to two phases as the temperature is raised, this behaviour is called the lower critical solution temperature (LCST) behaviour (see Figure 3-2b) [Sperling, 1992]. This is basically opposite from UCST behaviour.

Figure 3-2c illustrates the combination of both upper and lower critical solution phase boundaries, seen most commonly in nonpolar polymer solutions [Kroschwitz, 1990].

Figure 3-2d shows the convergence of upper and lower critical boundaries for an immiscible system to form an hourglass-shaped phase boundary. This type of phase diagram is the common phase diagram for the commercial polymer alloys [Thongyai, 1990].

Figure 3-2e illustrates the existence of upper, lower, and quasilower critical phase boundaries. This type of phase diagram can be observed in polar polymer solutions, e.g. poly(acrylic acid)-dioxane [Kroschwitz, 1990].

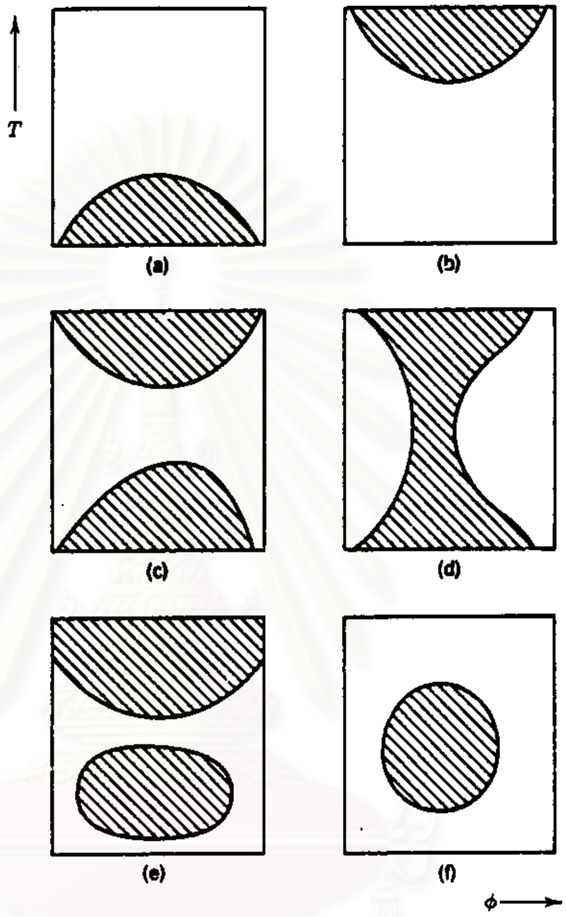


Figure 3-2 Schematic representation of six possible phase equilibria diagrams for binary mixtures in which the shaded areas represent phase separation [Kroschwitz, 1990].

Figure 3-2f shows the immiscibility loop with upper and lower critical phase boundaries inverted. The examples of this type of system are nicotine-water and poly(vinyl alcohol)-water [Kroschwitz, 1990].

3.6 Determination of Miscibility

To determine the compatibility of polymer blends, the variety of experimental techniques are used. Some techniques, such as calorimetric, dilatometric, dynamic mechanical, dielectric, are based on the determination of the number and the location of the glass transition temperatures (T_g). Other techniques are based on scattering or microscopy technologies. Melting point (T_m) depression is another method used to determine the miscibity. Each technique has its own advantages, resolutions, cost, difficulties, assumptions and availabilities.

Figure 3-3 [Gedde, 1995] presented a summary of different techniques used for the assessment of miscibility of polymer blends. It also suggested the suitability of each techniques in relation to the domain size of the blend.

3.6.1 Glass Transition Criteria for Compatibility

Glass transition temperature (T_g) is a characteristic of the amorphous part of a polymer. At T_g, a dramatic change occurs in the local movement of polymer chains which leads to large changes in a host of physical properties. These properties include density, specific heat, mechanical modulus and mecha-

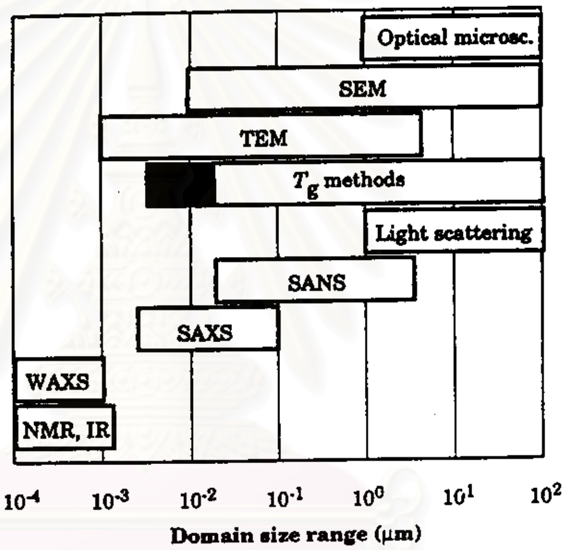


Figure 3-3 Size range covered by different experimental techniques for the assessment of miscibility [Gedde, 1995].

nical energy absorption and their dielectric and acoustical equivalents, rate of gas or liquid diffusion through the polymer, as well as many other properties [Brandup and Immergut, 1989]. Typically, polymer becomes glassy below its T_g and is rubbery above its T_g. A complete theoretical understanding of the T_g phenomenon is not yet available. The current theories can be divided into three groups: free volume theories, kinetic theories and thermodynamic theories [Gedde, 1995]. Although the glass transition phenomenon is mainly known for its presence in polymers, many low molecular weight materials show it too. Some examples are 2-methyl pentane, glycerine, network glass like SiO_2, electrolyte solutions and even metals [Eisenberg, 1993].

Measuring the T_g of a polymer blend is the most commonly used method for determination its miscibility. It is clear that a miscible system will show characteristic properties of a single phase. Hence, a single T_g, intermediate of the components' T_g can be expected for a miscible blend. In case of partial miscibility, two transitions that shift closer to each other occur. The immiscible systems will show two separate transitions with little change from the transition temperatures of its pure components. This method, however, can be used to study polymer miscibility as long as the two T_g-s are at least $20^{\circ}C$ different [Oiarzabal, 1993].

The value of T_g depends on the miscibility of the blend and its composition. At different composition, the miscible blend will have different T_g. There are many theories [Utracki, 1989] to predict the T_g of a miscible blend. One of the most well known theories is the Flory-Fox equation as shown in Equation 3-3 [Paul and Newman, 1978].

$$\frac{1}{T_g} = \frac{W_1}{T_{g,1}} + \frac{W_2}{T_{g,2}} \qquad (3\text{-}3)$$

where T_g = glass transition temperature of the mixture

W_i = weight fraction of the *i*th component

$T_{g,i}$ = glass transition temperature of the *i*th component

The Flory-Fox equation was derived on the premise that $T_{gi}\Delta C_{pi}$ (ΔC_{pi} is the change in specific heat asssociated with the glass transition of component i) was constant [Sperling, 1992].

3.6.1.1 Glass Transition Determination

There are many methods by which T_g of polymer may be determined. Examples are differential thermal analysis (DTA), thermal optical analysis (TOA), differential scanning calorimetry (DSC), dynamic mechanical, dielectric measurement, and dilatometry. Some of the more widely used methods of T_g measurement in polymer blends are described below [Walsh, 1985]:

3.6.1.1.1 Differential Scanning Calorimetry (DSC)

The T_g is usually determined by a differential scanning calorimetey (DSC). DSC is the technique that monitors enthalpy changes (heat flow into or out) of a material (sample and reference) as a function of temperature or time. The sample and the reference are heated or cooled at a constant rate. The resulting temperature difference signal can then be recorded versus time or sample temperature [Fava, 1980]. An inflection in the plot is observed at the T_g because an increase in the specific heat of the polymer is accompanied by the increased molecular motion.

This technique has the advantage of small sample requirements (typically 5-20 mg), rapid measurement blend and high sensitivity.

The DSC method was selected for the determination of blend miscibility in this study.

3.6.1.1.2 Dynamic Mechanical Spectroscopy

Dynamic mechanical measurements have been widely used in the study of polymer compatibility. With this technique, a dynamic modulus can be measured as a function of temperature over a range of frequencies. From traditional torsion pendulum measurements, the dynamic shear loss modolus (G″) and the dynamic shear storage modulus (G′) may be obtained as a function of temperature at a nominal frequency in the vicinity of 1 Hz.

The torsion pendulum consist of an inertial source (disk or rod) connected to a polymer specimen which is firmly fixed at the other end. The inertial source is angularly displaced and released, allowed the specimen to vibrate freely. The resultant damped sinusoidal wave is then determined using a suitable recording device [Olabisi, 1979].

The T_g (or T_g's) of the blends is defined as the temperature corresponding to the maximum in G″ or tanδ (tanδ = G″/G′) at the main relaxation, which marks the onset of main chain segmental mobility corresponding to the glass transition.

This technique has more stringent sample requirements than calorimetry, that only films or fibers (i.e. not powders) made from the blends can be studied, However it is sometimes preferred because of a widely held belief that it is more sensitive than calorimetry.

3.6.1.1.3 Dielectric Relaxation

The electrical properties of polymers are analogous to mechanical properties in that the dielectric constant, ε', is similar to compliance, the dielectric loss factor, ε'', is similar to mechanical loss, and the dielectric strength is analogous to tensile strength. The dielectric loss factor and the dissipation factor, $\tan\delta$ $(\varepsilon'/\varepsilon'')$, are of primary interest as they are commonly used to ascertain polymeric transition such as the glass transition. The ε', ε'' can be measured by placing the sample between parallel plate capacitors and alternating the electric field [Sperling, 1992]. The experimental advantage of obtaining transition data from electrical measurements over dynamic mechanical testing is in the ease of changing frequency.

The major disadvantage is the difficulty in determining the transitions of nonpolar polymers. Generally, nonpolar polymers will require slight modification, such as oxidation, to provide sufficient polarity to resolve adequately secondary loss transition as well as glass transition in blends [Olabisi, 1979].

3.6.1.1.4 Dilatometry

The earliest used method of determining T_g in polymers, dilatometry, has been infrequently employed in blend studies because of the greater speed and versatility of modern thermal analysis instrumentation.

A dilatometer consists of a glass bulb with an attached small capillary. The dilatometer is then placed in a temperature bath, and the temperature changed at a uniform rate so that a plot of volume as a function of temperature is obtained. An inflection piont indicates the position of the glass transition [Eisenberg, 1993].

In contrast to DSC, dilatometry requires larger samples and more time and care in sample preparation and measurement.

3.6.2 Scattering

A quick but not totally reliable method to determine that a polymer blends forms a single phase or multiphase is by its transparency [Olabisi, 1979]. Discontinuous domains in the polymer blends are often large enough to refract light, forming a translucent or an opaque blend when two transparent polymers are mixed. In a miscible one-phase blend of two amorphous polymers (transparent polymer), no domains are present to refract light and, hence, the blend may be transparent.

By the scattering method, one may reach erroneous conclusions if

1. The refractive indexes of polymer A and polymer B are similar.
2. The domains are smaller than that of the wavelength of light, the light is not scattered, and a two phase blend can be transparent.
3. Either component of an initially transparent miscible blend later crystallizes, the blend may become opaque.

To improve this technique, the use of an x-ray and a neutron scattering provide much insight into the blend morphology. Furthermore, small-angle neutron scattering has emerged as a powerful tool for investigating many aspects of polymer blends [Olabisi, 1979].

3.6.3 Microscopy

Microscopy is the name given to a group of experimental methods which permit magnification of morphological structures to make details visible [Gedde, 1995]. Microscopy provides detailed information about miscibility and phase morphology, i.e. the actual geometry of the phases. The microscopic methods can be divided into three categories as follows:

3.6.3.1 Optical Microscopy

The optical microscope is obtained by two lens systems, referred to as the objective and the eyepiece. The objective generates a magnified real image of the specimen. The real image is further magnified by the eyepiece and a magnified real image is formed at the retina of the eye [Gedde, 1995].

Optical microscopy resolves structures down to about 1 μm. The sample may need staining prior to examination. In other cases, where the refractive index mismatch is sufficiently large, direct examination can be made in the microscope using phase-contrast as interference-contrast optical microscopy.

3.6.3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) uses the technique of a focus electron beam to scan the sample surface [Woodward, 1995]. The electron beam is controlled by lenses consisting of magnetic fields. Rotational symmetric electromagnets focus the electron beam in the same way as convex lenses do in optical microscopes [Gedde, 1995]. The polymer specimen to be examined by SEM was first coated with a thin layer of gold to provide a conductive layer.

Scanning electron microscope (SEM) provides more detailed information on the morphology; domains down to a size of 10 nm can be resolved. SEM is becoming the most popular method of observation of polymer blends. The great advantages of this technique are: rapidity, great depth of focus, relatively simple image interpretation, and ease of sample preparation.

From these reasons, SEM was selected for the studying of phase morphology of the blend in this study.

3.6.3.3 Transmission Electron Microscopy (TEM)

The transmission electron microscope is built according to the same principle as the optical microscope, with a condenser lens, an objective lens and a projector lens (the analogue of the eyepiece). A magnified image is obtained on a fluorescent screen or on a hairpin tungsten filament or a lanthanum boride (LaB_6) filament heated with a low-voltage source. The potential of the filament is highly negative and the electrons are accelerated towards an anode held at a small positive potential [Gedde, 1995].

Transmission electron microscopy (TEM) involves complex and tedious preparation of the samples necessary to reveal the microphase. But the resolution of TEM is superior to optical microscopy and SEM.

3.6.4 Melting Point Depression

The general equation for melting point depression is Nishi-Wang equation [Olabisi, 1979], as shown in Equation 3-4.

$$\frac{1}{T_m} - \frac{1}{T_m^o} = - \frac{RV_2}{\Delta H_2 V_1}\left[\frac{\ln \Phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)(1 - \Phi_2) + \chi_{12}(1 - \Phi_2)^2\right] \quad (3\text{-}4)$$

where

T_m = The experimental melting point

T_m^o = The equilibrium melting point

V_1, V_2 = The molar volume of diluent and polymer repeat unit

ΔH_2 = The heat of fusion of 100% crystalline polymer per mole of repeat unit

m_1, m_2 = The degree of polymerization for constituents 1 and 2

Φ_2 = The volume fraction of crystalline polymer

χ_{12} = The interaction parameter of the blends

The equilibrium melting point (T_m^o) of a polymer is defined as the melting point of a group of large crystals, each in equilibrium with the polymer melt. Hoffman and Weeks have proposed a way to obtain T_m^o [Fava, 1980].

For polymer mixture, m_1 and m_2 (the degree of polymerization for consistuents 1 and 2) are very large, thus

$$\frac{1}{T_m} - \frac{1}{T_m^o} = - \frac{RV_2}{\Delta H_2 V_1} \chi_{12} (1 - \Phi_2)^2 \tag{3-5}$$

For miscible blend of crystallizable polymers, the melting point (T_m) shifts to a lower value as predicted by Nishi-Wang equation (equation 3-5 indicates that a negative χ_{12} will yeild a melting point depression). On the other hand, the T_m of immiscible blend systems which have semicrystalline components, does not change (equation 3-5 indicates that a positive χ_{12} will yeild a melting point elevation).